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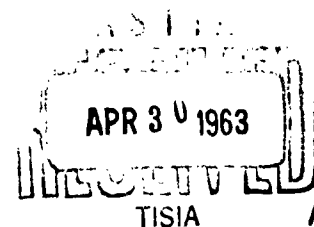
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Antiferromagnetic Behavior in Single Crystals

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The objectives of this research were a study of the antiferro-
magnetic transition and the antiferromagnetic state at low tempera-
tures. We believe that the general objectives of the work have
been met. In the material which follows we outline the work that
has been carried out by the nuclear resonance technique and by specific
heat studies. Each of these techniques has contributed information
about both the antiferromagnetic state and the antiferromagnetic
transition. However, in the case of nuclear magnetic resonance,
the principal contribution seems to have been in providing informa-
tion about the antiferromagnetic state while in the case of the
specific heat work the information it provides is largely concerned
with the antiferromagnetic transition.

Nuclear Resonance Studies

A study of the antiferromagnetic state involves determining
the orientation and distribution of magnetization within the crystal.
It is hoped that when a sufficient amount of information of this
type is available we will be in a position to better understand the
process of magnetic ordering which occurs in magnetic materials.
The nuclear magnetic resonance technique measures the internal
magnetic fields at sites which are occupied by preselected "probe"
nuclei in the crystal. The internal magnetic fields can be observed
either in the presence of an additional externally applied field,
or in zero external field. The method involving the use of an
external field is rather conventional and does not need any great
amount of review here. The vector sum of the internal and external

field must be such as to satisfy the Larmor resonance condition for the marginal oscillator which in this case is normally maintained at a fixed frequency. The external field is varied until a signal is observed and from the value of the external field, the frequency of the detector, and knowledge of the direction in which the external field is applied, one can determine both the magnitude and directions of the internal field.

The zero field method is novel in some aspects and since it has not been discussed elsewhere we consider it in a little more detail here. Each probe nucleus has an inherent Larmor frequency arising from the internal field at the nuclear site. This internal field arises from the magnetic ions which in our case are always at some distance from the probe nucleus. To determine the magnitude of the internal fields it is only necessary to vary the frequency of the marginal oscillator until the signals arising from the various internal fields are observed. The resonant frequencies are then carefully measured and by using the Larmor resonance condition one calculates the magnitude of the internal fields. To facilitate detecting the resonance signals we actually apply a very small slowly oscillating external field which sweeps the nuclear frequencies back and forth. This results in two signals on the oscilloscope. The two signals arise in the following manner. For every set of points in an antiferromagnetic crystal having a given value of the local field there exists another set of points related to the first by a symmetry operation of the crystal for which the internal magnetic field is of the same magnitude but reversed in direction. When the modulating field is increasing it combines with one set of

internal fields to produce one of the observed signals and when it
is decreasing it combines with the other set to produce the other
observed signal. If the frequency of the oscillator is such that
it corresponds exactly to the Larmor frequency dictated by the
magnitude of these two oppositely directed fields the two signals
coalesce. In this way we have an accurate method of setting the
oscillator when measuring the magnitude of the internal fields. To
measure the direction we set the detector frequency at a value
slightly above or below that which produces coalescence of the two
signals. It can be shown that if the orientation of the modulating/ field
is changed the two signals will most nearly coalesce when the
direction of the modulating field is along the direction of the
internal field. Thus the zero field method is capable of measuring
both the direction and magnitude of the internal fields. It is
faster and less inclined to distort the spin arrangement than the
external field method. Since however it is difficult to apply phase
sensitive detection techniques with the zero field method (particular-
ly when measuring directions) it is generally slightly less sensitive
than the external field method.

Having measured the internal magnetic fields it is necessary
to determine the particular nuclei with which they are associated.
In the crystals we have examined these nuclei were protons on the
waters of hydration. Unfortunately the structure as determined by
x-ray crystallography does not give the proton positions and con-
sequently their positions must be determined by an auxiliary
n.m.r. experiment. This experiment is done at room temperatures
where the perturbing effects of the magnetic ions in the crystal are

negligible. The orientation of the vector connecting the two protons
in the water molecule is determined by using the fact that the
dipole-dipole interaction between the protons is maximum when the
magnetic field is along the inter proton vector. Knowledge of the
interproton vector combined with the assumption that in the water
molecule the protons are 0.97 angstroms from the   oxygen
serves to determine the proton positions. One further step is still
necessary to associate the internal fields with specific protons.
This is accomplished by noting that on the resonance lines in the
antiferromagnetic state there appears a fine structure due to the
dipole-dipole interaction. The angular dependence of this dipole-
dipole interaction is compared with the angle dependence of the
dipole-dipole interaction of various water molecules as observed at
room temperature, and in this way the final association is made.
Having determined the internal fields at certain points in the
crystal, we now consider what may be inferred about their magnetic
structure. The most direct and simplest conclusions are those
concerning the magnetic symmetry group of the crystal. All magnetic
crystals, whether they be ferromagnetic or antiferromagnetic, can
presumably be cataloged into one of 1651 possible arrangements of
magnetic moments. The only exceptions to this rule seem to be
certain conducting antiferromagnets in which the variation of
magnetization is not compatible with the crystal structure. The
possible arrangements of magnetic moments in a magnetic crystal are
known as Schubnikov groups. Unfortunately no tables of these groups
were in existence when this work was started and we found it

necessary to prepare tables covering the symmetries of the crystals with which we worked. These tables are given in Technical Report 4. Generally the n.m.r. data only allows one to select several possible space groups. Furthermore selection of the magnetic space group does not provide any information about the direction of the spins in the crystal. The spin direction can be determined by measuring the magnetic susceptibility in a single crystal specimen. The susceptibility with the magnetic field perpendicular to the spin direction varies very little with temperature, while the susceptibility parallel to the spin direction decreases rapidly as the temperatures decrease. On the basis of the symmetry of the nuclear magnetic resonance data one can normally arrive at several possible spin arrangements. It remains to determine which of these corresponds to the physical situation and to also determine the detailed distribution of magnetic moment around the magnetic ion. If it were possible to measure the magnetic field everywhere in the unit cell, including the region within the ion, it would be possible to determine the distribution of magnetic moment by straight forward mathematical techniques. However the limited data provided by our experiments does not permit any such direct attack on the problem. What has been done is to assume a distribution magnetic moment, calculate the fields which it would produce, and compare these with the experimentally observed internal fields. In such a trial and error method one is guided by the possible magnetic symmetries of the crystal and by knowledge of the way the magnetic ions are bonded to their nearest neighbors. Nevertheless the program is extremely tedious and we have found it only possible by using high speed computing machinery.

The portion of the program outlined above which involves only
enumerating the space groups is relatively straightforward, and can
be carried out with the minimum amount of auxiliary experiments and
information. An example of this is the material lithium copper
chloride, which is discussed in Technical Report No. 2. The general
program is clearly much more complicated and has been carried through
in the case of only four salts, namely $NiCl_2.6H_2O$, $Ni\ Br_2.6H_2O$,
$Co\ Cl_2.6H_2O$ and $Co\ Br_2.6H_2O$. Not only was a full set of auxiliary
nuclear magnetic resonance and susceptibility studies required for
these salts, but also in the case of the bromine compounds it was
necessary to determine the required x-ray parameters. Since the
results of this work on these salts are not yet in publication, we
summarize some of the results here.

We find that the characteristics of the chlorine and bromine
salts are essentially the same provided the magnetic ion is the
same. The spins are parallel to the c axis in the cobalt salts
and parallel to the a' (perpendicular to c) axis in the nickel salts.
Symmetry considerations alone allow us to deduce from the n.m.r. data
that there are two permitted magnetic arrangements. These may be
described in terms of the arrangement of spins in the (001) planes.
In the first space group the spins in each successive plane are
reversed, but in the planes themselves they are all parallel. We
might call this an antiferromagnetic arrangement of ferromagnetic
planes. The other space group consists of a series of (001) planes
in which we have antiferromagnetic arrangement of spins. Thus the
two space groups are based on ferromagnetic and antiferromagnetic

planes respectively. When we attempt to fit the numerical values of the observed field by assigning distributions of magnetization, we find that only the space group based on antiferromagnetic planes give reasonable results and the space group is therefore determined. The distribution of magnetization which gives best results seems to be a distribution of magnetization which is nearly spherically symmetric but somewhat elongated along the bonds between the magnetic ions and the halogens.

A number of other crystals were examined and internal magnetic fields were measured. These include the antiferromagnetic Mn $Cl_2.4H_2O$ and the weak ferromagnetic Mn $(C_2 H_3 O_2)_2$. $4H_2O$. However in these materials the x-ray structure is not yet known and we are therefore not able to say much about the magnetic structure.

The Antiferromagnetic Transition

The antiferromagnetic transition is presumably a second order transition and as such should not exhibit any superheating or super-cooling. That is there should be no overlap of the antiferromagnetic or paramagnetic phases. We were therefore much suprised to find that in the mineral azurite it was possible to observe simultaneously a set of lines belonging to the paramagnetic state and a set of lines belonging to the antiferromagnetic state. The range of simultaneous observation was $0.2°$K. which is large compared to the Néel tempera-ture of $1.86°$K. A subsequent observation of the same phenomena at Leiden indicates that the result is not a function of the apparatus or of the sample. These results were reported in an informal

discussion at the International Conference on Magnetism at Kyoto. The essence of the theoretical discussion of this phenomena was that the peculiar behavior of azurite might be due to either strains in the crystal or in some way associated with the large amount of short range order which is found in the neighborhood of the transition temperature. Forstat had previously shown that the transition in lithium copper chloride is accompanied by even more short range order than in azurite, and therefore it was decided to examine the transition in this material very carefully. The region in which the two phases overlapped was examined and it was found that the temperature field over which the overlap occurred is much smaller than in azurite and amounts to only $.02^{\circ}K$. It would therefore seem that the short range order is not the governing factor in this problem. Since this work a number of other laboratories have examined the transition in antiferromagnetic materials and the results are in complete agreement with ours, although the width of the region in which the two phases overlap is generally nearer to that of lithium copper chloride than that of azurite. The result seems to be a fundamental one in that the paramagnetic antiferromagnetic transition is now perhaps the best studied second order transition. The experimental results indicate an overlap of phases which is not consistent with thermodynamic theory.

Specific Heat Studies

Studies on the specific heats of single crystals have been carried out in line with the proposed program of this contract. This work will be described by briefly summarizing the published results and some of the experiments which are not complete enough to warrant any clear cut interpretation.

1. Single crystals of Li Cu $Cl_3 \cdot 2H_2O$, grown from an aqueous solution at room temperature, have been examined by specific heat techniques in an adiabatic calorimeter. The temperature range covered was 2-9°K. A λ-type anomaly was observed at 4.4°K. corresponding to a paramagnetic-antiferromagnetic transition. Such a transition has also been observed by nuclear magnetic resonance techniques. An unusual feature of this transition is the very large entropy change associated with the short range ordering. Nearly half of the total entropy change was found to lie above the Néel temperature. In addition, evidence from these experiments indicate a ground state spin of 1/2 for the Cu^{++} ion since the magnetic entropy change from the data agrees within 2% of the expected value as calculated from R ln (2S + 1).

2. Specific heat studies have been made on single crystals of manganese acetate   Mn $(C_2 H_3 O_2)_2 \cdot 4H_2O$. Earlier work on the magnetic supceptibility of this substance indicated an unusual transition at approximately 3°K. The present experiments indeed show a transition at 3.2°K, but a very weak one. At the present time, it is not clear whether this transition corresponds to a paramagnetic-antiferromagnetic or paramagnetic-ferromagnetic ordering.

It is suggested that this may correspond to a weak ferromagnetic
transition of the Dzialoshinski type. This corresponds to a slight
canting of planes of spins. No definitive statement can be made in
connection with this at the present time. From these experiments
it has been possible to show the existence of some nuclear entropy.
The data show that the specific heat below $3.2^{\circ}K$ do not approach
zero as the temperature decreases, but rather drop to approximately
1 cal/mole deg at $2^{\circ}K$, remain constant down to $1.4^{\circ}K$ and then begin
to rise again. Such behavior has been observed in some ferrites,
and most recently in cobalt ferrite. By a least square fit of the
experimental points, it has been shown that the specific heat varies
as $1/T^2$, in accord with the theoretical predictions on the temperature
dependence of the nuclear specific heat, which, of course, arises
from the interaction of the nuclear magnetic moment and the magnetic
field set up at the nucleus by the orbital electrons. As for the
total magnetic entropy change in this transition, the data give a
result which is too small by a factor of 2 from the predicted value
based on a ground state spin of 5/2 for the Mn^{++} ion. This
descrepancy has not been completely resolved since at the present
it has not been possible to take data very much below 1.17°, where
possibly the nuclear contribution may add considerably to the over-
all magnetic entropy change.

3. In connection with the work on manganese acetate, some
specific heat measurements have been made on a mixed crystal of
manganese and cobalt acetate. Some crystals of this mixture were
grown at room temperature, and indicate a chemical composition of
manganese acetate with approximately 2% cobalt. It was of interest

to observe that the curve shows a transition (approximately the same size as pure manganese acetate) at a slightly lower temperature, i.e. $3^{\circ}K$ as compared to $3.2^{\circ}K$ for pure manganese acetate. This impurity depression of the transition temperature is in agreement with the work that has been done on the impurity doping of pure metals (Co, Mn, Ni, etc.). This work is still in the preliminary stage and should be considered for further experimentation.

4. Some work on single crystals of ferrous chloride tetrahydrate (Fe Cl_2 · $4H_2O$) indicates no transitions, either magnetic or crystallographic ordering down to $1.23^{\circ}K$, although the experimental curve begins to show a slight rise below $1.4^{\circ}K$. It has since been observed by other experimentors that there is indeed a transition but it lies below $1^{\circ}K$, a temperature which can not be attained by our present apparatus.

5. Since our previous experience has indicated that within a series of magnetic compounds with the same magnetic ion and isomorphous to one another it may be possible to observe magnetic transitions, it was thought worthwhile to examine ferrous bromide tetrahydrate (Fe Br_2 · $4H_2O$). Here one should expect (if indeed there is a magnetic transition) a higher transition temperature. Specific heat studies have been made on single crystals of this compound, and a transition was observed at $1.28^{\circ}K$. Subsequent work on this crystal by nuclear magnetic resonance techniques do not, at present, corroborate the existence of a transition. However, the nmr work is still not totally complete since some difficulty has been encountered in obtaining a reasonably strong signal. Furthermore, it

is very difficult to obtain good crystal specimens for the nmr experiments, and until one does, comparison of the specific heat work with the nmr work will have to be held in abeyance.

6. Experiments have also been conducted on a deuterated sample of manganese chloride. These crystals were grown from an aqueous solution of D_2O, producing crystals of Mn $Cl_2.4D_2O$. The interest in such crystals arose from work done by some Japanese experimentors on the paramagnetic susceptibility of Co $Cl_2.6H_2O$ and its deuterated salt. This earlier work showed no appreciable difference in the susceptibilities of these two salts, although one would have suspected that the hydrogen bonding should be different for these two conpounds. The specific heat work indicated a magnetic transition at $1.6^{\circ}K$ for Mn $Cl_2.4D_2O$ which does not differ appreciably from that for Mn $Cl_2.4H_2O$. However it was observed that the experimental values for Mn $Cl_2.4D_2O$ fall more sharply below the Neel temperature than they do for Mn $Cl_2.4H_2O$. It is suggested that the nuclear entropy contribution may be smaller for Mn $Cl_2.4D_2O$ than it is for Mn $Cl_2.4H_2O$. At the present that is about all we can say. Further work needs to be done to clarify this situation.

7. Some work has been done on Ni $SO_4.6H_2O$ and Cu $(NO_3)_2.3H_2O$ but nothing of especial interest has been observed here. These crystals show no abnormal behavior, with the specific heat simply decreasing steadily so the temperature decreases.

8. Single crystals of a nickel iodine compound (Ni$I_2.6H_2O$) have been examined.

The specific heat shows a slightly rounded maximum at

approximately $1.5^{\circ}K$. Such a shaped peak suggests the existence of a Schottky effect (the transitions involved in passing from an excited to a ground state for the Ni^{++} ion). Further work is being carried out in this analysis so that no definitive remarks can be made at the present time.

Published Papers and Technical Reports

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   510 (1962) (This is the published paper of the work reported
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3. Nuclear Magnetic Resonance in Sodium Thiosulfate Pentahydrate -
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   States - R. D. Spence and Z. M. El Saffar - J. Phy. Soc. of
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5. The Monoclinic and Orthorhombic Shubnikov Groups - R. D. Spence
   (Tech. Rept. 4)

Students Theses

A Nuclear Magnetic Resonance Study of $CoBr_2.6H_2O$ in the Antiferro-
  magnetic State - Paul W. Middents

Nuclear Resonance Studies of Antiferromagnetic Crystals in Zero
  Field - Doohee Kim

Heat Capacities of $LiCuCl_3.2H_2O$ and $FeCl_2.4H_2O$ in the liquid Helium
  Range - Donald R. McNeely

Specific Heat Studies of Mn $(C_2H_3O_2)_2.4H_2O$ and $FeBr_2.4H_2O$ in the
  Liquid Helium Temperature Range - Sister M. Charles J. Zinn

Students Supported by the Contract

Donald R. McNeely - M.S. Aug. 1961

Sister M. Charles J. Zinn - M.S. June 1962

Ivan O. Fisher - B.S. June 1962

Paul L. Lin - Ph.D. candidate

Norman D. Love - Ph.D. candidate

Warren Eisenberg - M.S. candidate

Doohee Kim - M.S. Mar. 1963

Paul W. Middents - M.S. Mar. 1963